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An On-surface Reaction Confined within a Porous Molecular Template

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Abstract: On-surface reactions based on metal-catalysed Ullmann coupling have been successfully employed to synthesise a wide variety of covalently coupled structures. Substrate chemistry and topology are both known to effect the progression of an on-surface reaction; offering routes to control efficiency and selectivity. Here, we detail ultra-high vacuum scanning probe microscopy experiments showing that templating a catalytically active surface, via a supramolecular template, influences the reaction pathway of an on-surface Ullmann-type coupling reaction by inhibiting one potential intermediate structure and stabilising another.

Metal-catalysed covalent coupling reactions performed in the solution phase result in the formation of new covalent bonds between molecular units. The study of reactions on surfaces, where the substrate itself may be employed as the catalyst for the reaction, has facilitated real-space imaging of the molecule-surface system by scanning probe microscopy (SPM) techniques; such as scanning tunnelling microscopy (STM) and non-contact atomic force microscopy (ncAFM). These techniques provide chemical identification of individual molecules^[1,2] and have allowed characterisation of molecular products, and intermediate states, on a level where the formation of individual chemical bonds can be resolved.^[3–5]

A wide-range of on-surface reactions have been studied by SPM techniques under ultra-high vacuum (UHV) conditions.^[6–12] Ullmann-type coupling reactions, where the C-C coupling of aryl halides gives rise to 0D, 1D and 2D covalently coupled structures, have been the focus of many studies and are observed to proceed on a variety of metallic substrates.^[13–16] In addition, confinement to a 2D surface offers the potential for novel regio- and stereo-selective reaction pathways which are not available in solution phase synthesis.

The reaction pathway for Ullmann coupling is of particular interest as it has been observed to proceed via an intermediate structure with metal adatoms from the substrate being incorporated between molecular units (see Fig. 1a). Such intermediate structures often bear similarities to metal-organic frameworks^[17–19] (MOFs) formed via alternative methodologies, but may be converted to a covalent structure by supplying additional thermal energy.^[20]

The mechanism by which C-C coupling proceeds is generally agreed to be a sequence of:^[8] (i) Catalytic cleaving of the C-X bond leading to the formation of a surface-stabilised radical species (forming a bond with a metal atom). (ii) Diffusing

radicals may meet and bond to the same metal atom – the intermediate state in the reaction. (iii) Elimination of the metal atom to form a new C-C bond between the molecular units.

The specific mechanistic role of the substrate atoms in the formation of the metal-organic intermediate and covalently bonded product has proven difficult to elucidate. Computational studies, employing density functional theory (DFT), investigating the progression of the on-surface reactions have predicted that the intermediate states are organometallic structures bound to substrate lattice atoms (pathway (1) in Fig. 1b),^[21] whereas metal-organic intermediates in experiments are frequently observed to contain adatoms in the same plane as the organic molecules^[20,22–25] (pathway (2) in Fig. 1b). Metal-organic structures formed via this mechanism have frequently been observed on Cu^[20,22,23] and Ag^[24] substrates, and only infrequently on Au.^[25] In general, for surfaces where the barrier for the initial catalytic cleaving of the C-X bond is large (e.g.

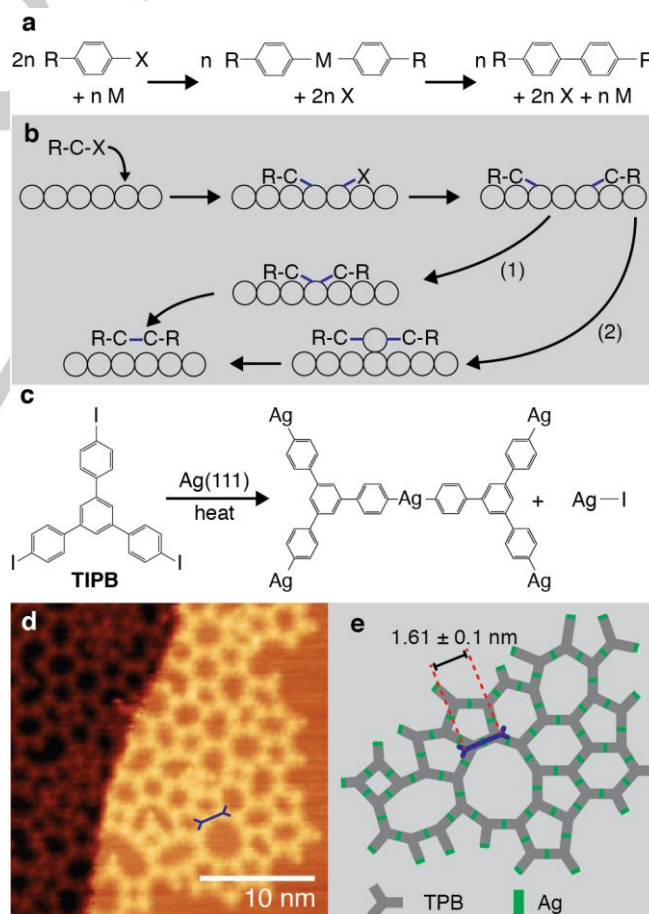


Figure 1. Non-templated reaction of TIPB on Ag(111). a Scheme of Ullmann-type coupling reaction via a metal-organic intermediate structure. b Two alternative pathways for the formation of a covalent product. c, Chemical structure of TIPB and scheme for formation of 2D-MOF. d, STM image showing extended 2D-MOF formed from TIPB on Ag(111). e, Structure of a region of the 2D-MOF. Image parameters: V(sample-bias)=+1.8V, I(set-point)=50pA.

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Au(111)) the metal-organic intermediate is seldom observed. Whereas, for a surface with a relatively low barrier for the C-X bond cleavage (e.g. Cu(111)) the intermediate is stable – with thermal annealing above room temperature (RT) required for conversion to the covalently bonded product. Additionally, recent work has focused on reaction kinetics^[26] and the chemical role of the halogen atoms in stabilising the intermediate structures.^[27]

The importance of the role of the substrate atoms is illustrated in work by Lewis *et al.* where bromobenzene was observed to undergo Ullmann coupling on Cu(111)^[28] and Co nanoparticles supported on Cu(111).^[29] On Cu(111) bromobenzene reacts to form organocuprate dimers, and it is postulated that Cu adatoms are extracted from the step-edge sites (extraction from terraces has also been observed in Ullman-type reactions on Au(111)^[25]). Conversely, for the same reactant molecule on Co nanoparticles the intermediate state was determined to be the debrominated molecules bound to Co atoms within the surface layer of the nanoparticle – subsequent addition of thermal energy resulted in direct conversion to the covalently bonded product. These two reactions highlight the two different pathways for an Ullmann type reaction (shown schematically in Fig. 1b); pathway 1 – via a metal-organic intermediate, pathway 2 – direct conversion of the surface-stabilised radical to the covalent product. The difference in reaction pathway for these two examples is potentially a consequence of the difference in; (i) surface mobility of the Co and Ag adatoms, and (ii) the energetics of step-edge and surface- vacancy creation - resulting in additional adatom species.

It is therefore apparent that the precise mechanism by which catalytic metal atoms interact with reactant molecules plays an important role in determining the pathway which the reaction proceeds. In this work we seek to influence the reaction pathway of an Ullman-type on-surface reaction by templating a catalytically active metal surface with a porous molecular array containing nanoscale 2D-cavities; limiting access to diffusive surface adatoms, and active-sites at step edges,^[2,30] in order to influence the reaction pathway.

The chemical reaction studied here is the catalytically activated formation of a 2D-MOF on a Ag(111) surface. The reactant molecule, 1,3,5-tris(4-iodophenyl)benzene (TIPB – chemical structure shown in Fig. 1c), contains three carbon-iodine (C-I) bonds and possesses a three-fold rotational symmetry. Following deposition of TIPB onto a Ag(111) sample held at RT, or elevated temperature (100 °C), STM images reveal formation of an extended 2D-MOF (Fig. 1d). Following catalytic cleavage of the C-I bonds to form a reactive species (a surface stabilised radical^[13] – in this case (1,3,5-tri(phenyl)benzene, TPB) – an extended porous 2D-MOF structure is formed with Ag adatoms incorporated within the framework (2D-MOF structure shown in Fig. 1e). The separation between vertices of the 2D-MOF is found to be 1.61 ± 0.1 nm (dimensions indicated in Fig. 1d – additional characterisation details given in Supporting Information), demonstrating that the network structure is indeed stabilised by metal-organic coordination interactions (C-Ag-C), in agreement with previous studies for similar systems (1.62 ± 0.1 nm^[24] – where the metal atoms are found to be in the same plane as the molecular units).

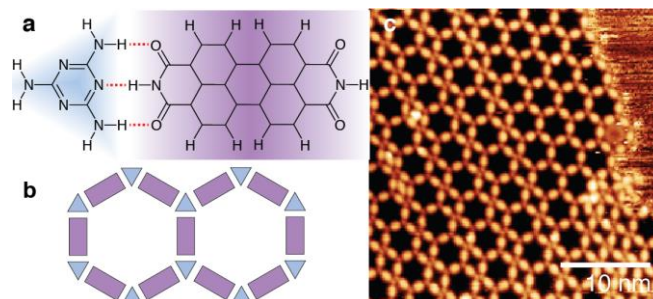


Figure 2. PTCDI-melamine porous hexagonal network on Ag(111). a, Chemical structures of melamine (left) and PTCDI (right) - directional hydrogen-bonds indicated. b, Schematic of hexagonal network. c, STM image showing hexagonal network formed from PTCDI-melamine on Ag(111). Image parameters: V(sample-bias)=+1.8V, I(set-point)=50pA.

This is in contrast to the dimensions expected for the covalently coupled product ($1.31\text{nm}^{[31]}$).

Although the three-fold symmetry of TIPB is suggestive of a preference for the formation of a hexagonal structure, the observed 2D-MOF exhibits a non-regular arrangement with cells of square, pentagonal, hexagonal, and higher-order polygonal symmetries (schematic showing a region of the observed cellular structure presented in Fig. 1e). Such a finding is in agreement with structures formed from a similar molecule with identical symmetry but different halogen chemistry (C-Br instead of C-I).^[31] Here we assign the Ag atoms incorporated into the MOF structure as being available from a reservoir of diffusing surface adatoms (i.e. diffusion of atoms from step-edges to form a 2D adatom gas^[32]). This is in agreement with our observation that no atoms are lifted from the terraces (e.g. no vacancy island generation on terraces^[33]); an alternative source of adatoms.

In order to explore the role of Ag adatoms in the progression of the reaction, and to investigate how we may influence the reaction pathway, we template the Ag(111) surface using a porous molecular overlayer. The template may potentially limit the number of reactant molecules which can interact and to reduce or remove access to Ag adatoms. One methodology for such templating is the use of self-assembled networks, where inter-molecular non-covalent bonding motifs (often based on hydrogen bonding or metal coordination) are used to drive the formation of porous molecular structures which can be tuned to give a variety of pore shapes and sizes.^[17,18,34,35] Here, the Ag(111) surface was templated using a porous hydrogen-bonded supramolecular network formed from the self-assembly of a perylene based unit (perylene-3,4,9,10-tetracarboxylic-3,4,9,10-diimide - PTCDI) and melamine (1,3,5-triazine-2,4,6-triamine); schematic and chemical structures shown in Figs 2a-b. The directional hydrogen-bonding motif between these two species is known to give rise to porous hexagonal networks on the Ag/Si(111)^[36] and Au(111)^[37–39] surfaces. Structures based on PTCDI and melamine have been previously shown to act as molecular traps for various species.^[34,36–41]

A templated Ag(111) surface was prepared via sequential deposition of PTCDI and melamine with subsequent annealing of the sample to ~ 80 °C. The chemical structure and an STM image of the templated substrate are shown in figure 2. The pore-pore separation of the network is measured to be 3.5 ± 0.2

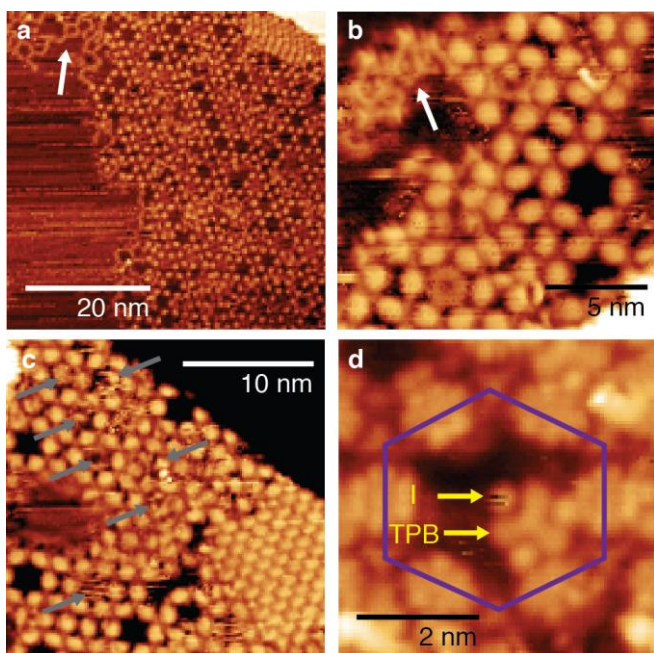


Figure 3. Confinement of an on-surface reaction within a PTCDI-melamine porous hexagonal network on Ag(111). a, STM image showing a domain of the PTCDI-melamine hexagonal porous network with co-deposited TIPB, a region of TPB-Ag is indicated by a white arrow. b, STM image showing PTCDI-melamine structure. MOF formed from TIPB present outside network. c, STM image with filled pores indicated with grey arrows – at RT trapped moieties diffuse continuously. d LT-STM image showing a single dissociated TIPB molecule trapped within a molecular pore. Image parameters: a-c $V(\text{sample-bias}) = -1.8 \text{ V}$, $I(\text{set-point}) = 50 \text{ pA}$, acquired at room temperature. d $V(\text{sample-bias}) = -1.8 \text{ V}$, $I(\text{set-point}) = 10 \text{ pA}$, acquired at $\sim 78 \text{ K}$.

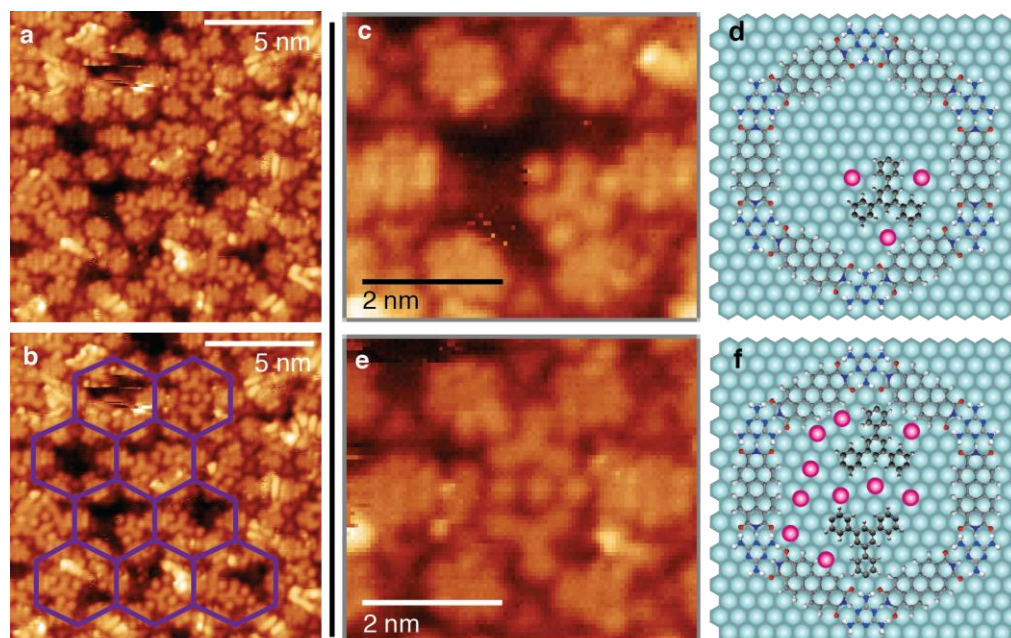


Figure 4. Host-guest architecture for filled pores. a-b STM images of the host-guest architecture. PTCDI-melamine structure highlighted in b. c,e Details of the STM images showing the arrangement of guest species within a network pore. Models for the positions of dissociated TIPB (TPB) and iodine atoms are indicated in d and f. Image parameters: $V(\text{sample-bias}) = -1.8 \text{ V}$, $I(\text{set-point}) = 10 \text{ pA}$, acquired at $\sim 78 \text{ K}$.

nm, identical to that for the network formed on Au(111).^[37] Following deposition of TIPB onto the templated Ag(111) surface STM images were acquired at room temperature. For regions of the surface outside of the network pores, i.e. the non-templated surface, small islands of 2D-MOFs are observed (indicated by white arrows in Fig. 3a-b). The separation of the vertices of these structures is found to be $1.63 \pm 0.1 \text{ nm}$, in good agreement with the structures deposited on the non-templated Ag(111) surface. A large proportion of the network pores are identified as filled following deposition of TIPB ($39 \pm 9 \%$). STM images acquired at RT reveal that the species trapped within the pores diffuse on a timescale faster than the STM acquisition time – resulting in a time-averaged image of the pore contents (filled pores indicated by grey arrows in Fig. 3c). To enable characterisation of the trapped species the templated substrate is transferred to a low-temperature system, via a ‘vacuum suitcase’, where STM images were acquired at $\sim 78 \text{ K}$ (see Supporting Information).

Figure 3d shows an STM image of a PTCDI-melamine hexagonal network pore within which a single TIPB molecule has been trapped. It is evident that the TIPB molecule has undergone the initial stage of the on-surface reaction, i.e. catalytic cleavage of the C-I bond, (position of a feature attributed to detached iodine atom indicated in Fig. 3d – discussed in more detail below).

A variety of features trapped within the pores of the PTCDI-melamine hexagonal network were identified (Fig. 4a-b). All of the observed TIPB species have undergone the first step of the catalytic process for the formation of the 2D-MOF, i.e. the carbon-iodine bonds within the molecule have been catalytically cleaved (confirmed by the reduced dimensions of TPB compared to TIPB and the change in appearance of the molecule – see SI).

The individual circular features arranged around the TPB molecule are attributed to iodine atoms which have been displaced from their original position in the intact molecule (Fig. 4c), in agreement with observations for other iodinated molecules.^[25,42] A detailed analysis of several pores allows us to determine that a maximum of three TPB molecules reside within any given pore (from a simple space-filling model the maximum pore occupancy is found to be three); range 0-3, average 1.4 ± 0.1 . A common arrangement within a pore is typified by the structure shown in figure 4c. A single TPB molecule can be identified, and is surrounded by three atomic sized features (attributed to

iodine atoms^[13,25,43]. The measured iodine-iodine separation of atoms within this structure is consistent with a model where each iodine atom is adsorbed at a three-fold hollow site (in agreement with similar halogenated molecular species on Cu(111)^[13] – see SI). Halogen atoms have previously been observed to be incorporated within extended metal-organic structures,^[23,44] but here isolated arrangements of a dehalogenated molecule appears to be stabilised by surrounding halogen atoms. A similar stabilising arrangement can also be observed with pores containing two TPB molecules (see Fig. 4e). In the majority of cases (~94 %) we find that the number of iodine atoms in a pore is equal to or greater than 3 times the number of TPB (i.e. on average 3.4 ± 0.1 iodine atoms per TPB molecule). This would be accounted for if additional iodine atoms were deposited during sublimation of TIPB (either due to an excess of iodine in the crystalline TIPB used for sublimation, or via breaking of the carbon-halogen bond during heating^[14]). We therefore infer that only a few, or indeed, no iodine atoms diffuse between neighbouring pores.

Templating the catalytically active Ag(111) surface with a porous molecular network provides additional information on the role of the substrate in the formation of the 2D-MOF structures observed on non-templated surfaces. Firstly, it is apparent that cleavage of the C-I bond for molecules contained within the network pores does not require interaction with metallic atoms removed directly from the substrate (no adatoms are removed from surface as evidenced by the lack of etch-pits) or at step-edges (porous molecular network inhibits diffusion to these active sites). Secondly, as ordered areas of the network are observed following the adsorption and reaction of TIPB, and as the formation of covalent bonds between TIPB and the network molecules is not apparent, we suggest that the template functions as a 'chemically inert wall' (although it is not possible to exclude the role of non-covalent interactions such as polarisation). We therefore conclude that, within the pore, substrate atoms may facilitate the breaking of the C-I bond via the previously suggested homolytic route^[45] involving; (1) partial filling of π^* orbital upon adsorption of TIPB, (2) charge transfer between π^* and σ^* orbitals (anti-bonding with respect to C-I bond), resulting in (3) cleavage of the C-I bond. The fact that we can discount the diffusion of TIPB to specific active sites on the substrate (e.g. step-edges^[2]), by confinement within the network pores, strongly suggests that adsorption mediated charge transfer to TIPB is the most likely route for C-I cleavage for molecules within the network pores. It should be noted that Ag adatoms are present on the pristine Ag(111) surface and therefore cannot be excluded from playing a role in C-I cleavage on the non-templated surface. However, our results indicate that the presence of Ag adatoms is *not* a necessary prerequisite for cleaving the C-I bond; as evidenced by the structures observed within the network pores.

It is interesting to note that no metal-organic structures are observed inside the pores when imaged at low temperature (~78 K); although there is sufficient volume within the pore for a bi-molecular metal organic species consisting of 1 Ag and two TPB molecules to be formed. This is in contrast to the case of the non-templated surface studied at RT; where extended networks of the 2D-MOF incorporating Ag adatoms are formed. We suggest two potential mechanisms for the inhibition of the

formation of the metal-organic structures, *either* by limiting the number of diffusing Ag adatoms within the pore *or* by altering the reactivity of the TPB reactive intermediate due to the proximity of the dissociated iodine atoms. In the first case, reduction in the number of surface adatoms within the template pore would inhibit the formation of the 2D-MOF; simply by removing one of the required components. Similar templates have previously been shown to inhibit the diffusion of atomic species.^[46,47] Alternatively, the presence of the iodine atoms within the pore may act to stabilise the reactive TPB intermediate (potentially via charge transfer between the adsorbed species or by sterically hindering the transition state geometry for the formation of the metal-organic structure). A combination of these effects may be responsible for the stabilisation of the $[TPB][I]_3$ intermediate species and inhibiting the formation of the 2D-MOF within the network pores.

In conclusion it has been demonstrated that an on-surface reaction can be performed within the pores of a templated catalytically active Ag(111) surface, and a different product is observed to that formed on the non-templated surface. The use of a templated surface offers insight into the reaction mechanism (diffusion to step-edges and removal of Ag atoms from surface layer are excluded for molecules within the network pores; with a likely preference for charge-transfer mediated bond scission), and the path of the reaction is influenced by confinement within the pores leading to the formation of a stabilised intermediate structure. Such a templating methodology allows an alternative route for control over on-surface reactions and potentially provides a tuneable approach (dependant on the size and shape of the pores) towards influencing the reaction pathway of on-surface synthesis.

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Keywords: heterogeneous catalysis • supramolecular chemistry • scanning probe microscopy • surface chemistry • templated reactions

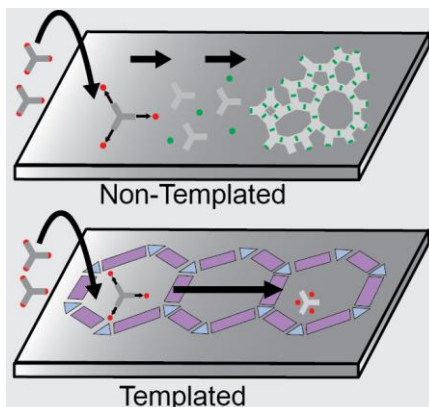
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COMMUNICATION

Tiny Templates. On-surface reactions can be performed on catalytic metal surfaces to combine molecular units into extended arrays. The structure of the catalyst, as well as its chemistry, is known to influence the shape of the product. Templating the catalyst with a porous self-assembled network gives rise to nanometer sized pores in which a chemical reaction can occur; leading to a different product to that formed on a non-templated surface.



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An On-surface Reaction Confined Within a Porous Molecular Template